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Adsorption and Decomposition of Chemisorbed Propylene on the Si(100)-(2x1) Surface: A Laser-Induced Thermal Desorption Study

by

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Adsorption and Decomposition of Chemisorbed Propylene on the Si(100)-(2x1) surface: A Laser-Induced Thermal Desorption Study

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Silicon Carbide

ABSTRACT

approx.

Deuterated propylene (C_3D_6) chemisorption and decomposition on the Si(100)-(2x1) surface has been studied in ultrahigh vacuum by using laser induced thermal desorption (LITD) and temperature programmed desorption techniques (TPD). Propylene was found to adsorb molecularly at 110 K and to remain as an undecomposed molecular adsorbate up to $\cong$ 500 K. As the surface temperature is increased, the propylene can both thermally desorb and decompose, ultimately producing a SiC thin film. LITD was used to study C_3D_6 and D_2 desorption as a function of surface temperature during temperature programming. Slow heating leads to strongly enhanced C_3D_6 decomposition compared to fast heating by laser irradiation. The decomposition of propylene is apparently a multistep process because deuterium is released from the chemisorbed propylene (and its fragments) over a temperature range from $\cong$ 450 to 850 K. D_2 desorption from the decomposition of C_3D_6 occurs at higher temperatures compared to that observed for chemisorbed deuterium.

1. INTRODUCTION

The adsorption and decomposition of hydrocarbons on silicon surfaces is a problem of both scientific and technological importance[1-12]. Few detailed chemical mechanisms are known for hydrocarbon chemical reactions on semiconductor surfaces. The technological importance of such studies relates to the production of thin films of SiC by CVD methods on silicon single crystal substrates. Decomposition of alkenes is particularly important in this respect. Bozack et al.[11-12] have previously determined that when a Si(100) surface is dosed with propylene and then heated, there is a 0.54 branching ratio, R, between molecular desorption and decomposition to SiC, based on Auger spectroscopic studies of surface

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carbon levels. The desorption of hydrogen was not reported in their work. In this study we have used laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) to show that propylene adsorbs molecularly and that the branching ratio of the extent of decomposition to the extent of molecular desorption can be decreased significantly using fast laser heating of the surface. The decomposition of propylene is a sequential fragmentation process in which deuterium atoms are delivered to the surface in several overlapping stages. Comparison of D_2 desorption from $C_3D_6(a)$ with D_2 desorption from D(a) indicates that the deuterium is more strongly bonded to the surface when carbon is present compared to pure deuterium on Si(100). These results will be compared to other studies of hydrocarbon reactions with Si(100) surfaces.

2. EXPERIMENTAL

The ultrahigh vacuum chamber, with a base pressure of 2×10^{-10} torr, used in this study has been described elsewhere[13-14]. Briefly, the system is equipped with an electron gun and four-grid optics for performing low-energy electron diffraction (LEED) and Auger electron spectroscopy. A differentially pumped quadrupole mass spectrometer (QMS) was employed to monitor the molecules desorbed from the surface, in both TPD and LITD experiments.

The Si(100) crystal (20x20x2 mm; p-type; B-doped; 10 Ω-cm) was mounted on a cooled manipulator as described elsewhere[13]. Thermal contact between the crystal and the liquid-nitrogen cooled sapphire mounting block was such that crystal temperatures of 110 K were readily attainable. The silicon surface was heated resistively, and accurate linear temperature ramps were achieved between 110 and 1000 K by using a chromel-constantan, type E thermocouple detector and a feedback circuit which controls the power delivered to the crystal. In situ cleaning by Ar^+ sputtering (1.5 keV, 6μA) for 60 min. and annealing the crystal surface to 1100 K for 30 min. resulted in a sharp (2x1) LEED pattern. The surface cleanliness was verified by Auger spectroscopy. After cleaning, no carbon signal was observed in the Auger spectrum. Given the signal-to-noise ratio of the spectrometer, the ratio C/Si $\lesssim$ 4 atom% in the depth of Auger sampling.

Adsorption of C_3D_6 was carried out by using a collimated capillary array doser, containing a microcapillary channel plate collimator[13]. The effusion rate was controlled by using a 2.8 micron diameter orifice in the vacuum line delivering gas to the collimated doser. Baratron capacitance manometers were used to monitor the pressure in the gas storage region behind the orifice so that the gas doses could be quantitatively controlled by noting the pressure and time during dosing. The conductance of the doser for C_3D_6 was measured to be 1.85×10^{13} molecules $s.^{-1}$ $torr.^{-1}$. Using the

geometry of the doser and crystal, we estimate that a fraction f = 0.81 of the emitted C_3D_6 is incident on the crystal[15]. C_3D_6 and CH_3CDCD_2 were obtained from MSD Inc., and were further purified by several freeze-pump-thaw cycles. Investigation of the gas purity using the mass spectrometer showed no evidence of contamination.

The quantities of propylene and deuterium desorbed were monitored using both LITD and TPD techniques. In the LITD technique the 308-nm output of a XeCl excimer laser ($\simeq$ 2.0 mJ/pulse) is incident at an angle $\theta_i = 75^o$ with respect to the surface normal. This serves to heat rapidly a 2.5 mm^2 elliptical spot on the 20x20 mm Si(100) surface and to desorb the propylene or deuterium from that spot. A total of 18 nonoverlapping spots can be studied during a single temperature programmed experiment. The desorbed propylene is detected with an apertured (17.5 mm diameter) and differentially pumped quadrupole mass spectrometer, whose ionizer is located on the line-of-sight from the Si(100) crystal at a distance of 4 cm.

During TPD experiments, a 3 mm aperture was used at the entrance to the mass spectrometer. Since the Si(100) surface was positioned approximately 2 mm from the aperture, only gas desorbing from the crystal center is observed. Desorption from extraneous surfaces of the crystal support assembly is not detected[16].

For some experiments it was desired to produce deuterium overlayers independent of any propylene decomposition. To do so, deuterium atoms were supplied to the surface via a hot tungsten filament (1640 K) which serves to dissociate D_2 gas in the chamber at a pressure of 1×10^{-6} torr.

3. RESULTS

In this section we present results obtained from the following experiments: (1). Propylene desorption studied using LITD; (2). Comparison of the branching ratio of the undecomposed propylene to the decomposed propylene by LITD and TPD; and (3). Isotopically substituted propylene studied using TPD.

Figure 1 shows the C_3D_6 QMS signal intensity observed upon laser irradiation of a Si(100) surface as a function of the surface temperature (0.35 K/s heating rate). Here the surface was dosed with 1.2×10^{14} C_3D_6 molecules/cm^2 prior to measurement. Each data point in Fig.1 corresponds to the laser desorption of propylene from a new spot on the silicon surface with no overlapping of the spots, and the total set of data in Fig.1 are from three independent experiments. There are two important features of these data; the relatively smooth

increase in the C_3D_6 LITD signal from 110K to 480 K and the sudden decrease beginning near 500 K. The increase in the LITD signal from 110 to 480 K is due to the fact that the LITD process becomes more efficient as the surface temperature increases. The laser pulse energy at which all of the propylene would desorb at an initial surface temperature of 110 K is close to that at which the silicon surface is ablated. Thus in these experiments the laser pulse energy was attenuated to prevent the silicon surface from being damaged, and at low surface temperatures not all of the propylene is desorbed upon laser irradiation in a single laser shot. This effect is also partially due to the fact that the laser irradiated spot on the surface has a nonuniform intensity pattern. (A second laser shot at 130 K results in a C_3D_6 pulse approximately half as intense as

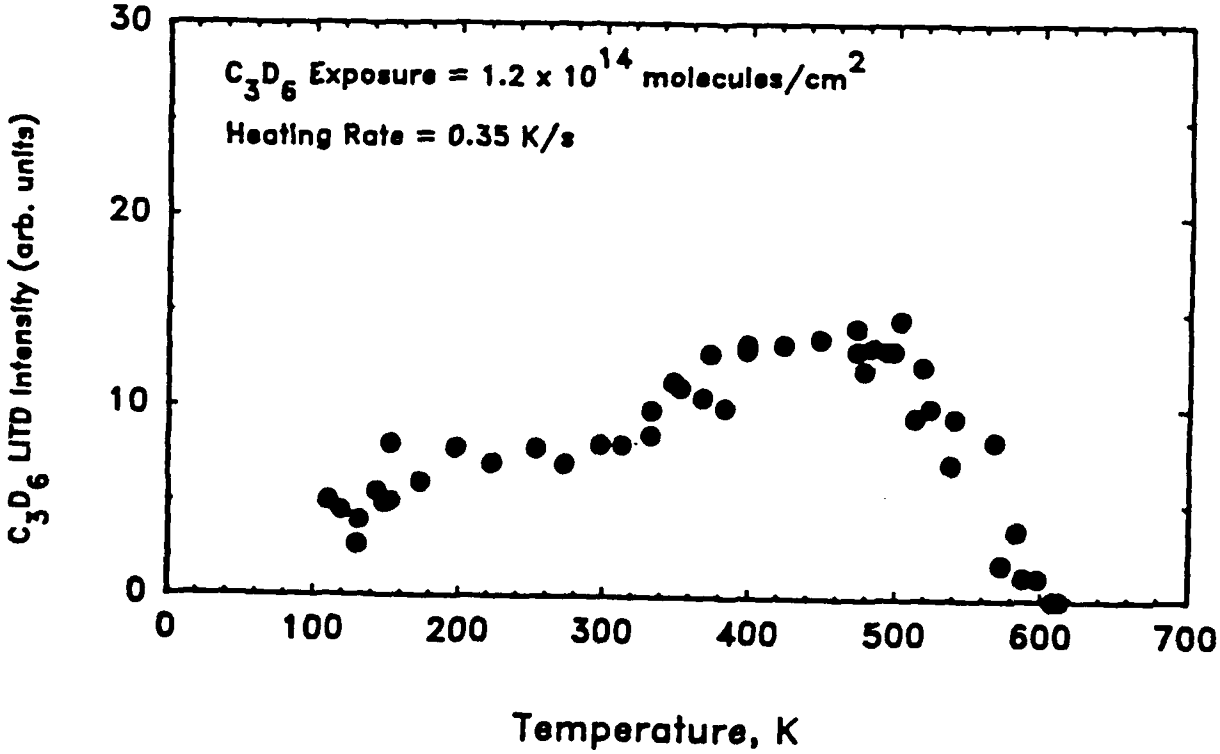

Figure 1. The C_3D_6 LITD signal is measured as the silicon surface is heated at 0.35 K/s. Each data point corresponds to a single laser shot incident upon a new spot on the surface. The propylene exposure is 1.2×10^{14} molecules/cm^2 at 110 K.

observed from the first pulse, while at 500 K, a second laser shot results in negligible C_3D_6 desorption.) That the LITD signal smoothly increases until 500 K is reached, and then suddenly decreases, indicates that the propylene remains molecularly adsorbed until 500 K at which point thermal decomposition and desorption of C_3D_6 begins to occur. During programmed heating in the temperature range 450 to 900 K no fragments of C_3D_6 were observed to form on the silicon surface by LITD. The only desorption signals observed between 5 and 50 amu were attributable to fragmentation of the desorbing C_3D_6 in the QMS ionizer.

Figure 2a shows data from five independent experiments in which the D_2 LITD signal as a function of surface temperature (0.35 K/s heating rate) is measured after the surface is dosed with 1.2×10^{14} C_3D_6 molecules/cm^2 at 110 K. It is interesting to note that from 250 to 500 K, the D_2 LITD signal is essentially constant, and relatively small. At 500 K, the temperature at which the propylene begins to decompose, there is a significant increase in the D_2 LITD signal that continues to 750 K. Above 750 K the D_2 LITD signal falls sharply due to D_2 desorption, but with a tail that extends to 850 K.

Figure 2b shows data from two independent experiments in which the D_2 LITD signal as a function of temperature (with a heating rate of 0.35 K/s as above) is measured after the surface was dosed with deuterium atoms up to saturation of the monodeuteride phase[14]. The qualitative features are similar to those observed in Fig.1 for C_3D_6 LITD, and quite different from those of Fig. 2a in which the deuterium desorbed by LITD originates mainly from the thermal decomposition of C_3D_6 molecules during temperature programming. The D_2 LITD signal from pure D(a) in Fig. 2b increases smoothly from 110 to 715 K, and then falls sharply as D_2 desorbs during temperature programming. No D_2 LITD signal is observed after a temperature of 800 K is reached. The efficiency of D_2 LITD simply increases with temperature until slow thermal desorption eliminates the overlayer.

Figure 3 shows the C_3D_6 and D_2 thermal desorption spectra (0.35 K/s heating rate) for C_3D_6 adsorbed on the Si(100) surface. The C_3D_6 was initially adsorbed at 110 K. At $\simeq$ 540 K molecular propylene desorbs at its maximum rate. (The C_3D_6 desorption peak temperature shifts to slightly higher temperatures as coverage is increased.) Molecular D_2 desorbs at its maximum rate at 765 K, and there is a significant tail at higher temperatures that is not observed when the surface is dosed only with deuterium atoms[14]. The integrated area of the D_2 peak is much larger than that of the molecular propylene peak, but the sensitivity to D_2 is much larger than to C_3D_6[17]. The actual propylene desorption/propylene decomposition branching ratio, R, based on the yield of C_3D_6 and D_2 is 0.7 from the data shown in Fig.3[17]. A series of measurements using heating rates from 0.35 K/s

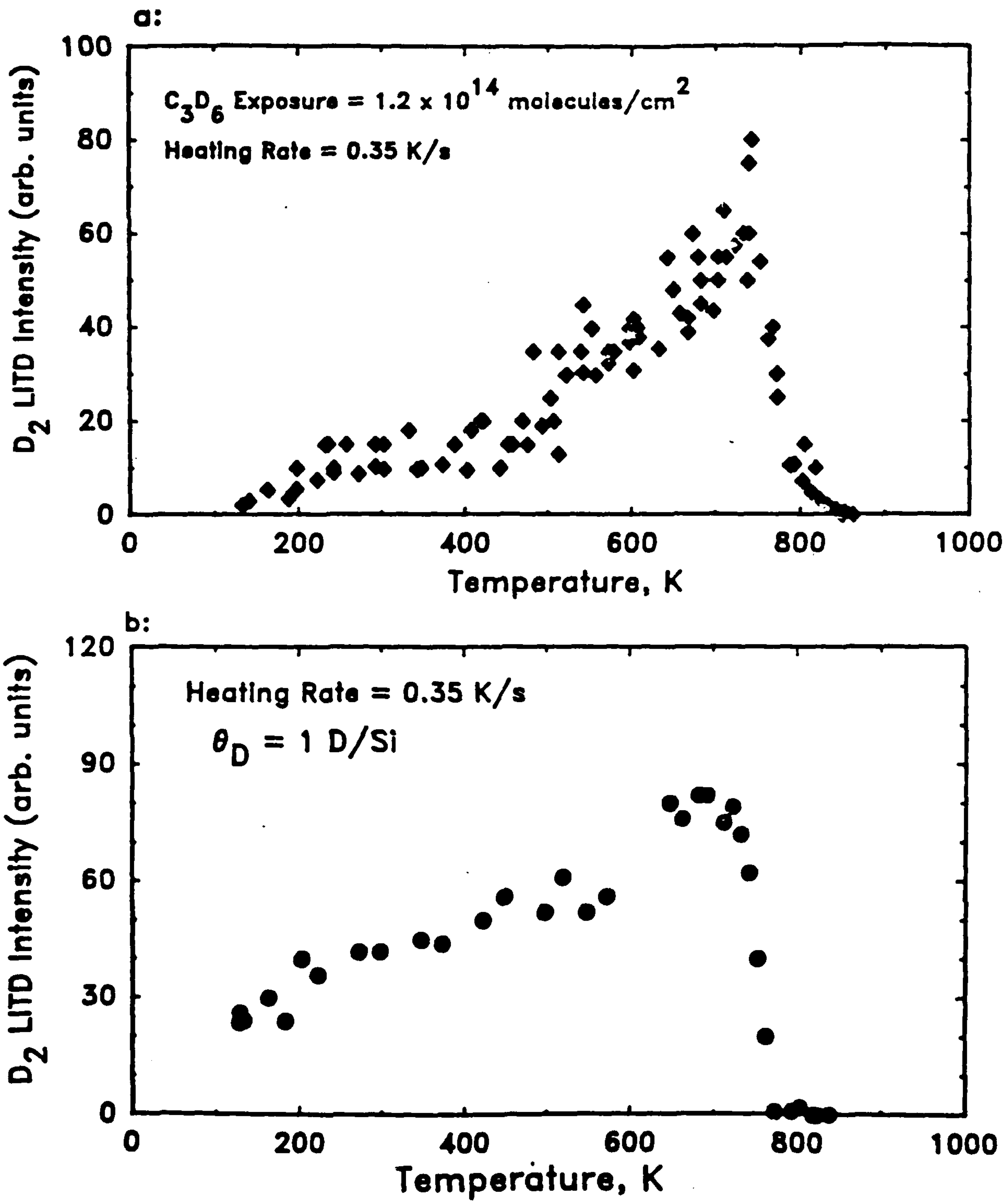

Figure 2. D_2 LITD signal as a function of surface temperature with a 0.35 K/s heating rate.
a: The surface was initially dosed with 1.2 x 10^{14} C_3D_6 molecules/cm^2 at 110 K.
b: The surface was initially dosed with deuterium atoms to saturation of the monodeuteride phase.

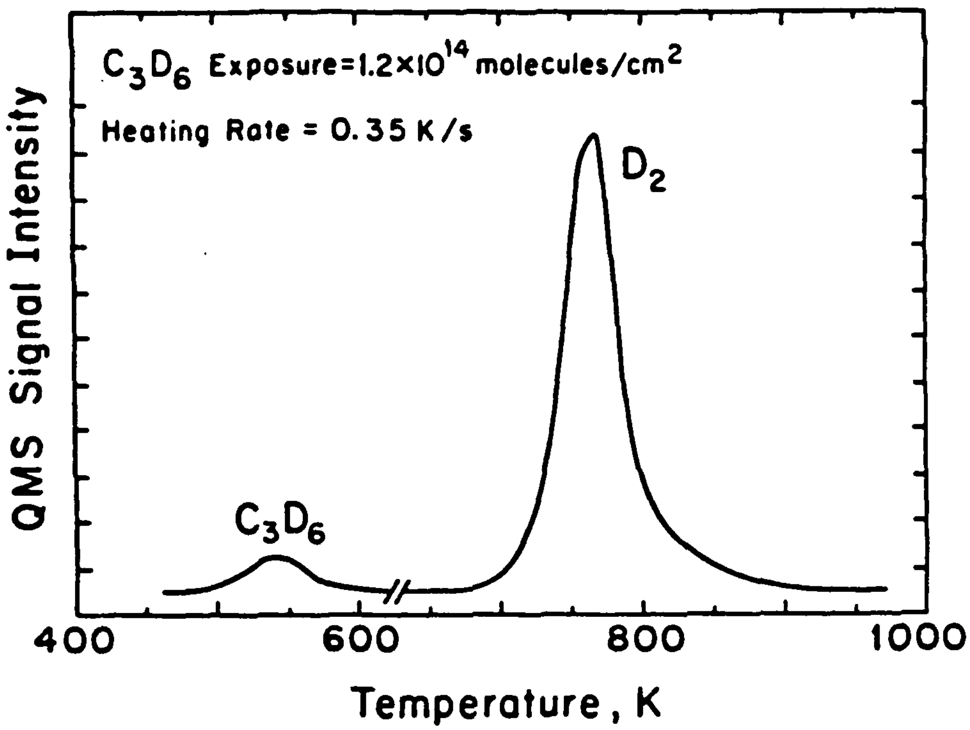

Figure 3. TPD spectra of C_3D_6 and D_2 desorbing from a Si(100) surface with a heating rate of 0.35 K/s. The surface was dosed with 1.2×10^{14} C_3D_6 molecules/cm^2 at 110 K. Below 650 K no deuterium was observed to desorb, while above 650 K no propylene was observed to desorb.

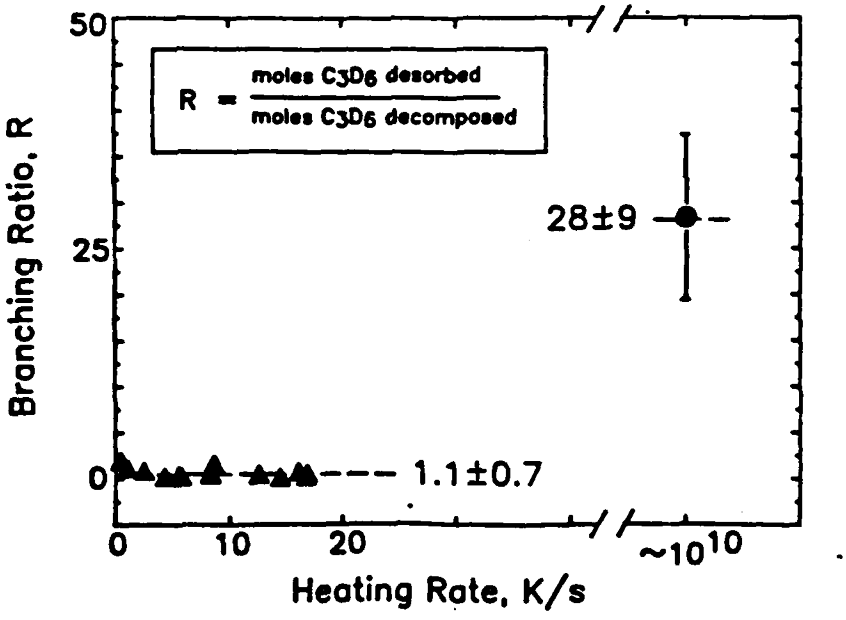

Figure 4. The change in the branching ratio, R as the heating rate is changed from slow TPD heating (0.35 - 18 K/s) to fast laser heating ($\simeq 10^{10}$ K/s). R = moles of C_3D_6 desorbed/moles of C_3D_6 decomposed.

to 18 K/s yield values for R in the range R = 1.1±0.7 as shown in Fig.4.

The change in the branching ratio, R, between molecular desorption and decomposition of C_3D_6 as the heating rate is changed from several K/s (TPD) to $\simeq 10^{10}$ K/s (LITD) is substantial. This is also shown in Fig. 4 in which R from the TPD curves is plotted as a function of heating rate, and R obtained from the LITD signals is shown for comparison. For the TPD experiments, R = 1.1±0.7 while R = 28±9 for fast laser heating at several different initial crystal temperatures below the desorption temperature of C_3D_6[18]. The error limits represent the reproducibility of the data. As will be further discussed below, the large increase in the branching ratio for fast laser desorption compared to slow temperature programmed desorption strongly supports our interpretation of Fig.1; that the propylene remains molecularly adsorbed up to 500 K. LITD may therefore be used as shown in Fig.1 to estimate the propylene coverage fairly accurately, since little C_3D_6 decomposition occurs upon rapid laser heating.

An independent measurement of R for slow heating rates can be obtained from the magnitude of the D_2 signal from a known coverage of deuterium, (Fig.2b) to the D_2 signal from the C_3D_6 decomposition (Fig.2a). From these data R is estimated to be 0.8±0.5 over the temperature range 600-700 K. This value, and the 1.1±0.7 value obtained from the more direct TPD measurement, are both consistent with the value R = 0.54 obtained in the Auger spectroscopy study[11-12].

Since the desorption/decomposition branching ratio is quite different for propylene and ethylene (see below), it seemed reasonable to propose that the propylene decomposition rate is somehow increased by the loss of hydrogen atoms from the methyl group. For this reason TPD studies were performed for C_3D_6 and CH_3CDCD_2. Figure 5 shows the thermal desorption spectra (2.5 K/s heating rate) for both C_3D_6 and CH_3CDCD_2 initially adsorbed at 110 K. Both the isotopes desorb at 575 K and the peak shapes look quite similar. From these results it appears that the isotope of hydrogen that is attached to the methyl group does not strongly influence the propylene desorption kinetics via a kinetic isotope effect, as would be expected if desorption were an independent kinetic process. Since propylene desorption competes with propylene decomposition, these results indirectly indicate that propylene decomposition does not exhibit a kinetic isotope effect on the methyl group.

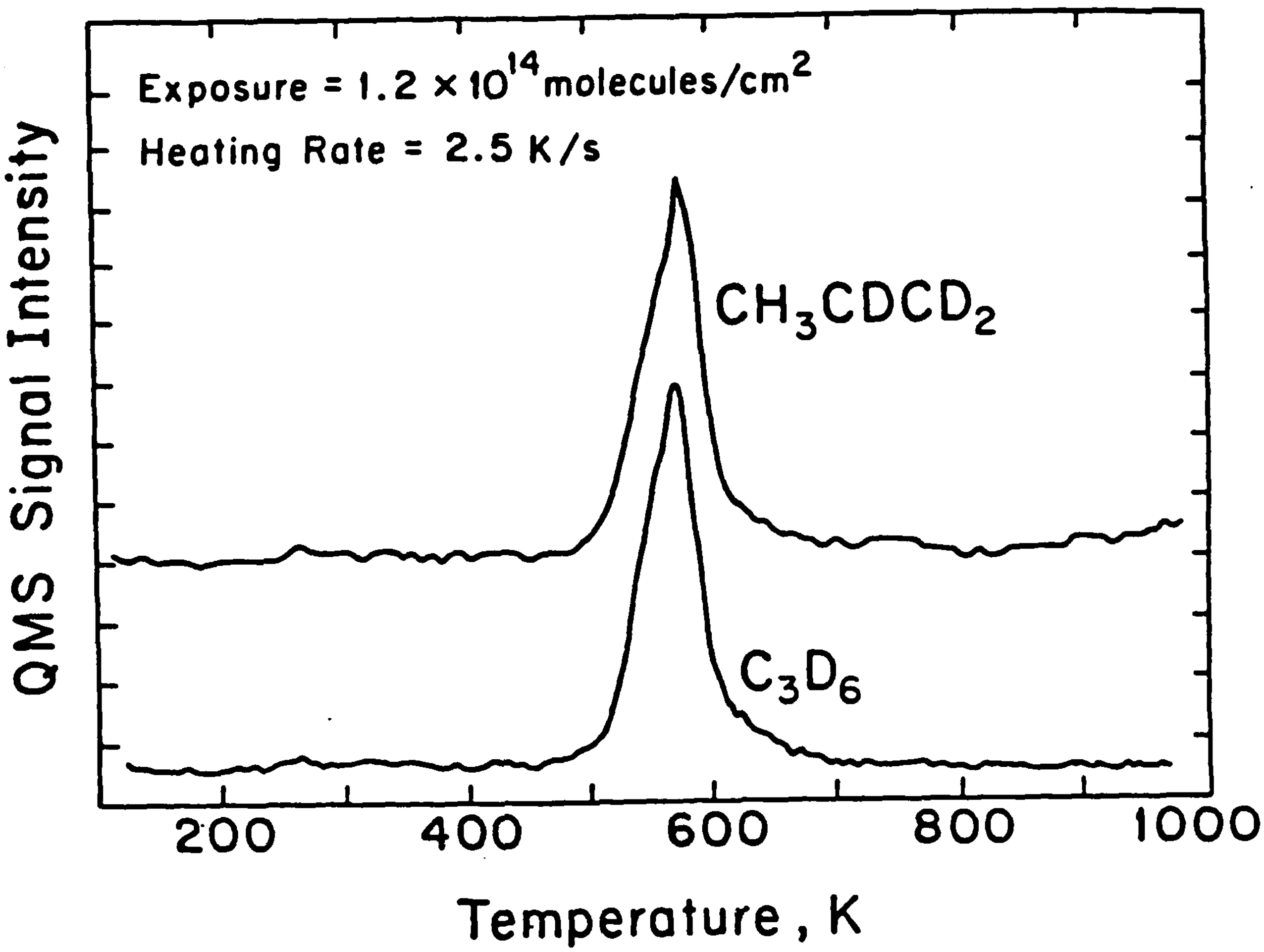

Figure 5. The thermal desorption spectra of C_3D_6 and CH_3CDCD_2 adsorbed on the Si(100) surface. The peak desorption temperature in both species is 575 K at a heating rate of 2.5 K/s.

In summary, we have presented results for LITD and TPD of chemisorbed propylene from the Si(100) surface. The laser irradiation of the propylene-covered surface has shown that propylene is molecularly adsorbed on the Si(100) surface up to $\simeq$ 500 K. LITD and TPD each produce both molecular propylene desorption and propylene decomposition resulting in D_2 desorption. However, the desorption / decomposition branching ratio is 28±9 for fast laser heating as compared to only 1.1±0.7 for slow TPD heating. Deuterium substitution for hydrogen atoms in the methyl group does not change the propylene desorption kinetics.

4. DISCUSSION

Though several experimental investigations have been performed in order to understand the bonding of alkenes to semiconductor surfaces the details of the interaction are still far from being completely understood. The adsorption of unsaturated hydrocarbon molecules on the Si(100) surface is of interest due to the production of SiC thin films formed during the thermal decomposition of these adsorbed species. The π bonding system in unsaturated hydrocarbon molecules is the active center for chemisorption on the Si(100) surface as originally postulated by Bozack, et al.[19]. Nishijima et al.[8-9] and Cheng et al.[20] have proposed that the carbon atoms in acetylene and ethylene bond to a silicon dimer unit via di-σ bonding across the C-C double bond. More recently Taylor et al.[21] have suggested a slightly modified scheme for the bonding. They propose that acetylene and ethylene adsorb via a mobile precursor state and that the final di-σ attachment results in cleavage of the Si-Si dimer bond. Thermodynamic arguments have been shown to favor such di-σ bonding over a mono-σ alternative[21]. A similar mechanism probably applies to the bonding of propylene to the Si(100). This is consistent with our observation that the propylene moiety is preserved until $T \simeq 500$ K. The initial chemisorption involves breaking the π bond of the propylene with no dissociation of the molecule.

Upon heating the propylene-covered silicon surface, a fraction of the propylene molecules thermally desorb and the remainder dissociate to produce C_xD_y species on the surface. Eventually, all of the deuterium originating from C_3D_6 thermal dissociation desorbs leading to the onset of SiC formation. From previous Auger studies, it has been shown that approximately 35% of the adsorbed propylene desorbs thermally while the rest decomposes[11-12]. Our present results are consistent with this ratio within our ability to calibrate our mass spectrometer sensitivity to C_3D_6 and D_2 desorption, and to reproducibly measure the branching ratio.

Not all alkene hydrocarbons dissociate to the same extent upon heating when they are chemisorbed on a silicon surface. In the case of ethylene, one study found that $\simeq$ 95% of the adsorbed ethylene desorbs molecularly from the Si(100) surface[22], while another study found somewhat smaller fractional desorption[8]. This suggests that the larger extent of propylene decomposition compared to ethylene decomposition is influenced by the presence of the methyl group on the alkene. This motivated us to compare the TPD rates of CH_3CDCD_2 and CD_3CDCD_2 as shown in Fig. 5. No substantial effect of isotope substitution at the methyl group is observed.

The absence of any desorbable (by LITD) intermediate species on the surface after propylene desorption suggests that the propylene decomposes to form C_xD_y species which are strongly bonded to the surface. The fact that a significant increase in the D_2 LITD signal is observed above 500 K as the propylene decomposes, combined with the fact that D_2 continues to be observed above $\simeq$ 750 K, indicates that deuterium is gradually lost from carbon-containing fragments over a large temperature range. This has been verified from TPD studies where the peak desorption temperature for D_2 from C_3D_6/Si(100) is approximately the same as that of D_2 from D(a)/Si(100), but a high temperature D_2 tail is observed when C_3D_6 is the source of deuterium. Also, when more propylene is adsorbed onto a carbon-containing silicon surface, several D_2 peaks are observed in the TPD spectra above 800 K as compared to the single D_2 peak observed in Fig. 3 from pure C_3D_6 with peak maximum at 765 K [23]. This confirms that most of the D_2 observed in Fig. 3 comes from the silicon surface while the high temperature tail is associated with deuterium bonding to carbon, or a carbon-induced enhancement of deuterium bonding to neighboring silicon atoms.

The rate of surface heating strongly affects the branching ratio between molecular desorption and decomposition. Fast laser heating significantly enhances the C_3D_6 desorption channel as seen in Fig.4. This implies that the desorption channel has a large prefactor in its rate law compared to the decomposition channel. Decomposition dominates at lower heating rates due to a smaller activation barrier. Such effects have previously been discussed for other systems by Hall and Bares[24] and by Zare and Levine[25].

5. SUMMARY

We have used the LITD and TPD methods to study the adsorption and desorption of propylene on the Si(100)-(2x1) surface. Upon heating the surface, the adsorbed propylene desorbs in one reaction channel and decomposes by another, leading to the onset of formation of a SiC film[11-12]. The LITD studies have shown that propylene adsorbs on the Si(100) surface molecularly. The extent of propylene decomposition to form SiC overlayers is much larger for slow TPD heating, where $R = 1.1 \pm 0.7$ than for fast LITD heating, where $R = 28 \pm 9$. These results are consistent with the previously proposed di-σ bonding of C_3D_6 to the Si_2 dimer site. Using LITD we have also shown that the decomposed propylene forms C_xD_y fragments on the surface at surface temperatures above 500 K which continuously lose deuterium atoms to the silicon surface as the surface temperature increases. Below 800 K most D_2 desorption from C_3D_6 occurs from deuterium adsorbed on the silicon surface. Above 800 K, especially at high carbon coverage, D_2 desorbs from the carbon fragments, or from silicon sites influenced by carbon atoms.

6. ACKNOWLEDGEMENT

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7. REFERENCES

(1). S. Nishino, J.A. Powell, and H.A. Will, Appl.Phys.Lett. 42, 460, 1983.

(2). A. Addamiano and J. Sprague, Appl.Phys.Lett. 44, 525, 1984.

(3). A.H. Mahan, B. Von Roedern, D.L. Williamson, and A. Madan, J.Appl.Phys. 57, 2717, 1985.

(4). H.J. Kim, R.F. Davis, X.B. Cox, and R.W. Linton, J.Electrochem.Soc., 134, 2269, 1987.

(5). F.W. Smith, Surf.Sci., 80, 388, 1979.

(6). F. Bozso, J.T. Yates, Jr., W.J. Choyke, and L. Muehlhoff, J. Appl.Phys. 57, 2771, 1985.

(7). H. Froitzheim, U. Kohler and H. Lammering, J.Phys. C19, 2762, 1986.

(8). J.Yoshinobu, H.Tsuda, M.Onchi, and M.Nishijima, J.Chem.Phys. 87, 7332, 1987.

(9). M. Nishijima, J. Yoshinobu, H. Tsuda, and M. Onchi, Surf.Sci. 192, 383, 1987.

(10). P.Klimesch, G.Meyer, and M.Henzler, Surf.Sci. 137, 79, 1984.

(11). M.J.Bozack, W.J.Choyke, L.Muehlhoff, and J.T.Yates,Jr., Surf.Sci. 176, 547, 1986.

(12). M.J. Bozack, P.A. Taylor, W.J. Choyke, and J.T. Yates, Jr., Surf.Sci. 179, 132, 1987.

(13). M.J.Bozack, L. Muehlhoff, J.N. Russell,Jr., W.J. Choyke, and J.T. Yates,Jr., J.Vac.Sci.Technol. A 5(1), 1, 1987.

(14). K. Sinniah, M.G. Sherman, L. Lewis, W.H. Weinberg, J.T. Yates,Jr., and K.C. Janda, Phys.Rev.Lett., 62, 567, 1989; J.Chem.Phys. (submitted).

(15). C.T. Campbell and S.M. Valone, J.Vac.Sci.Technol. A3, 408, 1985; A.Winkler and J.T. Yates, Jr., J.Vac.Sci.Technol. A6, 2929, 1988.

(16). V.S. Smentkowski and J.T. Yates, Jr., J.Vac.Sci.Technol. A7(6) 3325, 1989.

(17). The QMS was calibrated for sensitivity by measuring the mass 4 signal under dynamic pumping conditions for an ion gauge reading of 2.1 x 10^{-9} Torr of D_2, and the mass 48 signal for an ion gauge reading of 2.1 x 10^{-9} Torr of C_3D_6. The D_2/C_3D_6 ion gauge sensitivity ratio was taken to be 0.1 (from the Varian manual). Since the mass 4/mass 48 QMS signal ratio was 70, the overall D_2/C_3D_6 sensitivity ratio is 7 for the QMS.

(18). The ratio suggested here is only approximate and was obtained by accounting for the sensitivities of both the QMS ionizer and the ion gauge, as shown in Ref. 17.

(19). M.J. Bozack, P.A. Taylor, W.J. Choyke, and J.T. Yates, Jr., Surf.Sci. 177, L933, 1986.

(20). C.C. Cheng, R.M. Wallace, P.A. Taylor, W.J. Choyke, and J.T. Yates, Jr., J.Appl.Phys. (accepted).

(21). P.A. Taylor, R.M. Wallace, C.C. Cheng, W.H. Weinberg, M.J. Dresser, W.J. Choyke, and J.T. Yates, Jr., Surf.Sci. (to be submitted).

(22). C.C. Cheng, W.J. Choyke, and J.T. Yates, Jr., Surf.Sci. (accepted).

(23). From results obtained in this laboratory.

(24). R.B. Hall and S.J. Bares in Chemistry and Structure at Interfaces, edited by R.B. Hall and A.B. Ellis, pp. 85-149, VCH Publishers, 1986, and references therein.

(25). R.N. Zare and R.D. Levine, Chem.Phys.Lett., 136, 593, 1987.

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